JP11-080707

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CLAIMS

[Claim(s)]
[Claim 1] (1) The constituent for polish characterized by being the constituent for polish which comes to contain at least one kind of cation chosen from the group which consists of at least one kind chosen from water, (2) abrasives, (3) carbonate ion, the bicarbonate, and the group that consists of carbonic acid and (4) ammonium ion, alkali-metal ion, and each alkaline-earth-metal ion, and the total amount of the cation of (4) being 0.001-0.15 mols/l.
[Claim 2] The constituent for polish according to claim 1 which is at least one kind of abrasives chosen from the group which abrasives become from a silicon dioxide, an aluminum oxide, cerium oxide, titanium oxide, silicon nitride, a zirconium dioxide, and a manganese dioxide.
[Claim 3] The constituent for polish given in either of claims 1 or 2 whose contents of abrasives are 0.1 - 40 % of the weight on the basis of the weight of the constituent for polish.
[Claim 4] The constituent for polish given in any 1 term of claims 1-3 which is at least one kind of cation chosen from the group which a cation becomes from NH4+, Li+, Na+, K+, Be2+, Mg2+, and calcium2+.
[Claim 5] The constituent for polish given in any 1 term of claims 1-4 whose total amount of a cation is 0.005-0.1 mols/l.
[Claim 6] The constituent for polish given in any 1 term of claims 1-4 whose total amount of a cation is 0.01-0.075 mols/l.
[Claim 7] The constituent for polish given in any 1 term of claims 1-6 whose total amounts of a total carbonic acid which consist of carbonate ion, bicarbonate, and carbonic acid are 1/2 in a mole ratio to said cation. [200-2]
[Claim 8] (1) At least one kind chosen from water, (2) abrasives, (3) carbonate ion, the bicarbonate, and the group that consists of carbonic acid, And are chosen out of the group which consists of (4) ammonium ion, alkali-metal ion, and each alkaline-earth-metal ion. The polish approach of a semiconductor wafer characterized by performing surface flattening processing of a semiconductor wafer using the constituent for polish whose total amount of the cation of (4) it is the constituent for polish which comes to contain at least one kind of cation, and is 0.001-0.15 mols/l.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the polish approach of the suitable semiconductor wafer for surface flattening processing of the suitable constituent for polish for surface flattening processing of the device wafer especially in semiconductor industry etc., and a device wafer about the constituent for polish used for polish of various industrial products, such as a semi-conductor, a photo mask, various bases for memory hard disks, and synthetic resin, or the member of those.
[0002] in more detail, in polish of the silicon-dioxide film which is an insulator layer for the interlayer insulation film and isolation to which the CMP technique (detail postscript) is applied conventionally, this invention forms the polish front face excellent in the homogeneity in a wafer at the same time a big polish rate is obtained -- it can make -- the constituent for polish applicable to an advanced device formation technique -- and polish approach Seki is carried out.
[0003]
[Description of the Prior Art] The so-called advance of high-tech products including a computer in recent years is remarkable, and the components used for this, for example, ULSI, and ****** high integration and improvement in the speed are being enhanced. In connection with this, as for the design rule of a semiconductor device, detailed-ization progresses every year, the depth of focus in a device manufacture process becomes shallow, and the surface smoothness required of a pattern formation side is becoming severe.
[0004] Moreover, although compaction of the wire length by multilayering of a device is performed in order to cope with increase of the wiring resistance by detailed-izing of wiring, the level difference on the formed front face of a pattern has been becoming an issue as a failure of multilayering.
[0005] In performing such detailed-izing and multilayering, it is required in that process to perform flattening on the front face of a request for removing a level difference, and a spin-on glass, resist etchback, and other flattening methods were used as this technique until now.
[0006] However, by such technique, although partial flattening is possible, it is in a difficult situation to attain global pre nari ZESHON (perfect flattening) required of a next-generation device, and flattening (it is called "CMP" Chemical Mechanical Polishing and the following) by mechanical mechanochemical-polishing processing which was, carried out and combined physical polish and chemical polish is examined increasingly current.
[0007] The technical technical problem which hits carrying out flattening of the silicon-dioxide film which is an insulator layer for an interlayer insulation film or isolation using such a polish technique is raising productivity by grinding the field which carries out flattening processing at making homogeneity the neither more nor less and the big polish rate of the machining allowance by polish.
[0008] Conventionally, the constituent for polish containing the basic compound chosen from fumed silica, water and a potassium hydroxide, ammonia, and others has been used for polish of the silicon-dioxide film currently used for the insulator layer for an interlayer insulation film or isolation. When using such a constituent for polish, a polish rate can be enlarged if the quantity of the addition of a basic

compound is increased.
[0009] This is because chemical scouring is used in such polish processing. Chemical scouring will mean that the silicon-dioxide film becomes easy to receive removal by polish according to the effectiveness of the basic compound which is a chemical polish accelerator in response to chemical pervasion, if the above-mentioned polish processing is taken for an example. That is, in the above-mentioned polish processing, by increasing the quantity of the addition of a basic compound, a chemical operation increases and the whole polish rate becomes large.
[0010]
[Problem(s) to be Solved by the Invention] However, although usually comparatively a lot of basic compounds are included and the polish rate of need level was maintained in the conventional constituent for polish which was described above as far as this invention persons get to know, in the homogeneity of a polished surface, it could not be made sufficiently satisfactory level, but there was still room of amelioration. Therefore, establishment of the polish approach of the constituent for polish compatible in sufficient polish rate and the homogeneity of a polished surface and the semiconductor wafer using it was desired.
[0011]
[Means for Solving the Problem]
[Summary of the Invention]
The constituent for polish of <summary> this invention is at least one kind of cation chosen from the group which consists of at least one kind chosen from (1) water, (2) abrasives, (3) carbonate ion, the bicarbonate, and the group that consists of carbonic acid and (4) ammonium ion, alkali-metal ion, and each alkaline-earth-metal ion. It is the constituent for polish which becomes by ******, and is characterized by the total amount of the cation of (4) being 0.001-0.15 mols/l.
[0012] Moreover, the polish approach of the semiconductor wafer of this invention (1) At least one kind chosen from water, (2) abrasives, (3) carbonate ion, the bicarbonate, and the group that consists of carbonic acid, And are chosen out of the group which consists of (4) ammonium ion, alkali-metal ion, and each alkaline-earth-metal ion. It is the constituent for polish which comes to contain at least one kind of cation, and is characterized by performing surface flattening processing of a semiconductor wafer using the constituent for polish whose total amount of the cation of (4) is 0.001-0.15 mols/l.
[0013] The polished surface the constituent for polish of <effectiveness> this invention had the large polish rate, and homogeneity excelled [polished surface] in coincidence can be made to form.
[0014] Furthermore, the polish approach of the semiconductor wafer of this invention can make the polish front face excellent in the homogeneity in a wafer able to form, and can raise the productivity of a semiconductor wafer.
[0015] [Concrete explanation of invention]
Suitable abrasives to use as abrasives in the constituent for polish of <abrasives> this invention are chosen from a silicon dioxide, an aluminum oxide, cerium oxide, titanium oxide, silicon nitride, a zirconium dioxide, and the group that consists of a manganese dioxide.
[0016] In this invention, it has and that from which the manufacturing method of colloidal silica, fumed silica, and others and description differ recognizes variety existence at the silicon dioxide which can be.
[0017] There are alpha-alumina, delta alumina, theta alumina, kappa alumina, and a different thing like other gestalten also in an aluminum oxide. Moreover, there are some which are called a fumed alumina from a manufacturing method.
[0018] It sees in cerium oxide from a thing trivalent from the oxidation number, a tetravalent thing, and crystal system, and there is a thing of hexagonal system, a tesseral system, and a face-centered cubic system in it.
[0019] It sees in titanium oxide from crystal system, and there is a thing of titanium monoxide, 3 oxidization 2 titanium, a titanium dioxide, and others in it. Moreover, there are some which are called a fumed titania from a manufacturing method.
[0020] Silicon nitride has alpha-silicon nitride, beta-silicon nitride, amorphous silicon nitride, and a different thing like other gestalten.

[0021] A zirconium dioxide is seen from crystal system and has monoclinic system, tetragonal system, and an amorphous thing. Moreover, there are some which are called fumed zirconia from a manufacturing method.
[0022] A manganese dioxide is seen in gestalt and has alpha-manganese dioxide, beta-manganese dioxide, gamma-2 manganese oxide, delta-2 manganese oxide, epsilon-2 manganese oxide, eta-2 manganese oxide, and others.
[0023] These things can be combined and used for the constituent of this invention at arbitration if needed. When combining, especially the how to combine or rate to be used are not limited.
[0024] The above-mentioned abrasives grind a polished surface-ed according to an operation [mechanical / as an abrasive grain]. among these, generally 5-500nm of 10-200nm of particle size of a silicon dioxide comes out preferably with the mean particle diameter called for from the specific surface area measured with the BET adsorption method. moreover, generally an aluminum oxide, a zirconium dioxide, titanium oxide, silicon nitride, and 10-5,000nm of 50-3,000nm of particle size of a manganese dioxide come out preferably with the mean particle diameter called for from the specific surface area measured with the BET adsorption method. furthermore, the particle size of cerium oxide is the mean particle diameter observed by the scanning electron microscope, and, generally comes out 50-3,000nm preferably 10-5,000nm.
[0025] There is a between title of the surface roughness of the ground front face being large when the mean particle diameter of these abrasives is large across the range shown here, or a scratch occurring, and conversely, if smaller than the range shown here, a polish rate becomes extremely small and is not practical.
[0026] the content of the abrasives in the constituent for polish comes out one to 30% of the weight more preferably 0.1 to 40% of the weight on the basis of the weight of a constituent. If remainder has few contents of abrasives, the mechanical operation by abrasives will become weak, a polish rate will become small, when many [to remainder / conversely], it becomes impossible to maintain homogeneity distribution, constituent viscosity may become excessive, and handling may become difficult.
[0027] The constituent for polish of <carbonate ion, bicarbonate, and carbonic acid> this invention comes to contain at least one kind chosen from carbonate ion, the bicarbonate, and the group that consists of carbonic acid. As for carbonate ion and the bicarbonate, it is [among these] common to make it generate in the constituent for polish by dissolving the carbonic acid compound which dissolves in water and emits carbonate ion or the bicarbonate, i.e., carbonic acid, and its salt. Moreover, in this invention, since a main solvent is water, if a carbon dioxide is directly introduced into water, carbonic acid and the above-mentioned ion will generate.
[0028] The thing of arbitration can be used for the carbonic acid compound to be used if effectiveness of this invention is not spoiled. It is desirable that it is at least one kind of compound specifically chosen from the group which consists of potassium carbonate, an ammonium carbonate, a sodium carbonate, potassium sodium carbonate, a lithium carbonate, carbonic acid beryllium, a magnesium carbonate, a calcium carbonate, a potassium hydrogencarbonate, an ammonium hydrogencarbonate, a sodium hydrogencarbonate, and a carbonic acid hydrogen lithium. When a metal ion takes into consideration in these the effect and others which are given to a semiconductor device, especially ammonium-carbonate, ammonium-hydrogencarbonate, potassium carbonate, and potassium-hydrogencarbonate ** is desirable. Moreover, since an unnecessary metal ion is not introduced into the constituent for polish, it is also desirable to use a carbon dioxide. The salt (or carbon dioxide) of these carbonic acid can also be used together at a rate of arbitration.
[0029] In the constituent for polish of this invention, although the concentration of the total carbonic acid which are carbonate ion, the bicarbonate, and the total amount of carbonic acid is not limited unless the effectiveness of this invention is spoiled, it is desirable that the concentration of a total carbonic acid is 1/2 in a mole ratio to the total amount of the below-mentioned cation as a relative amount with the cation mentioned later, and it is desirable that it is especially 1/1. [200-2] [100-1] Although it is in the inclination for a polish rate to become large by making concentration of a total carbonic acid high, since the dispersibility of abrasives may get worse when it increases too much, cautions are required.

[0030] Although it is more desirable to the constituent for polish of this invention to introduce carbonate ion or the bicarbonate into the constituent for polish by using a water-soluble (soluble) carbonic acid compound from points, such as handling nature, it is possible to use, if dissolving into the constituent for polish is possible even if it is a poorly soluble compound. In other words, the ratios of the concentration of the aforementioned total carbonic acid and the total amount of a cation are the carbonate ion which is dissolving, the bicarbonate, and an amount based on carbonic acid, and it is not necessary to take into consideration the carbonic acid compound which exists in a constituent with a solid-state, without having dissolved by having added the amount more than the solubility of the compound. Moreover, as for an insoluble carbonic acid compound, it is desirable to remove, since it may become the cause of the surface discontinuity of a scratch or others.

[0031] The constituent for polish of <cation> this invention comes to contain a specific cation. In the constituent for polish of this invention, when used, these cations are the aforementioned carbonate ion, the bicarbonate, carbonic acid, or independent, and promote scouring according to an operation [KEMIKARU / as a polish accelerator].

[0032] The cation used in this invention is at least one kind of cation chosen from the group which consists of ammonium ion, alkali-metal ion, and each alkaline-earth-metal ion. The ion (henceforth "inorganic alkali ion") chosen from the group which consists of NH4+, Li+, Na+, K+, Be2+, Mg2+, and calcium2+ among these cations is desirable, and when the effect which it has on a vice with a semi-conductor is taken into consideration, NH4+ and especially K+ are desirable. Such ion is introduced into the constituent for polish by usually dissolving the basic compound which emits the aforementioned inorganic alkali ion into the constituent for polish. Although it will not be limited especially if the basic compound used here does not spoil the effectiveness of this invention, at least one kind of compound specifically chosen from the group which consists of a potassium hydroxide, ammonium hydroxide, a sodium hydroxide, a lithium hydroxide, hydroxylation beryllium, a magnesium hydroxide, and a calcium hydroxide is mentioned. These basic compounds can also be used together at a rate of arbitration. Moreover, about the above-mentioned basic compound, when metal ions other than the aforementioned inorganic alkali ion use the thing of very few high grades, since an impurity metal ion can be decreased in the constituent for polish, it is desirable.

[0033] although the content of the aforementioned inorganic alkali ion of the constituent for polish of this invention changes with classes of basic compound to be used -- the whole quantity of the constituent for polish -- receiving -- 0.001-0.15 mols/l. -- 0.01-0.075 mols [/] 0.005-0.1 mols /come out l. more preferably l. Although there is an inclination for a polish rate to become large by increasing the quantity of the content of said inorganic alkali ion, when many, it is in the inclination for the homogeneity of a polished surface to get worse. Furthermore, since the degree of amelioration to a polish rate etc. becomes small and may produce an economical demerit, cautions are required.

[0034] The constituent for polish of <constituent for polish> this invention makes water mix and distribute the above-mentioned abrasives with desired content generally, and is prepared by carrying out the specified quantity dissolution of carbonate ion, the bicarbonate, the compound that emits at least one kind chosen from carbonic acid, and the compound which emits the aforementioned inorganic alkali ion further. The method of distributing or dissolving these components underwater is arbitrary, for example, it agitates with a wing formula agitator, or it is distributed by ultrasonic distribution. Moreover, the mixed sequence foreword of each of these components is arbitrary, and may perform first whichever of the dissolution of distribution of abrasives, and a carbonic acid compound or a basic compound, and may perform both to coincidence.

[0035] Moreover, on the occasion of preparation of the constituent for polish of this invention, various kinds of well-known additives may be added further the purpose which attains quality maintenance and stabilization of a product, the class of workpiece, processing conditions, and if needed on other polish processings.

[0036] That is, the following are mentioned as a suitable example of the additive added further.

(b) Celluloses, for example, a cellulose, a carboxymethyl cellulose, Hydroxyethyl cellulose and others,

(b) water solubility alcohols, For example, ethanol, propanol, ethylene glycol, and others, A surface

active agent, for example, alkylbenzene-sulfonic-acid soda, the formalin condensate of naphthalenesulfonic acid, (Ha) and -- in addition to this -- (**) -- the organic poly anion system matter, for example, a ligninsulfonic acid salt, and polyacrylate -- and -- in addition to this -- (**) -- water soluble polymers (emulsifier), for example, polyvinyl alcohol, -- and -- in addition to this -- a (**) germicide, for example, sodium alginate, -- and -- in addition to this .

[0037] Moreover, although a thing is included said bottom as abrasives, a carbonic acid compound, and a basic compound in addition to the abrasives contained to the constituent for polish of this invention there, a carbonic acid compound, and a basic compound, it is also possible to be the purposes other than the application of abrasives or a polish accelerator, for example, to use the thing of inside to others as further additive for sedimentation prevention of abrasives.

[0038] it usually comes out of the constituent for polish of this invention that pH is set to 4-10 by said addition of a principal component carried out. Although pH of the constituent for polish is changed by addition of various kinds of auxiliary additives, in order to make the effectiveness of this invention discover, it is desirable that pH is 4-10. Therefore, when pH of the constituent for polish shifts from the range of 4-10, it is desirable to add an acid or alkali and to adjust pH. Moreover, even if pH is within the limits of this, it is [other being reasons, for example, the preservation stability of the constituent for polish, being / of a polish object / the physical properties, and] sometimes desirable for it to be alike and to adjust pH more nearly further in addition to this.

[0039] In addition, although the constituent for polish of this invention can be applied to the base material of arbitration, such as various industrial products, such as a semi-conductor, a photo mask, various bases for memory hard disks, and synthetic resin, or a member of those, it is desirable to use for surface flattening processing of the device wafer especially in semiconductor industry etc.

[0040] Moreover, the constituent for polish of this invention can be prepared as a comparatively high-concentration undiluted solution, can carry out storage or transportation, and it can also be diluted and used for it at the time of actual polish processing. When the above-mentioned desirable density range was indicated as a thing at the time of actual polish processing and it takes such operation, it cannot be overemphasized that it becomes a more high-concentration solution in the condition of carrying out storage or transportation. Moreover, it is desirable to be manufactured with such a condensed gestalt from a viewpoint of handling nature. In addition, the concentration mentioned above indicates not the concentration at the time of such manufacture but the concentration at the time of use about the constituent for polish.

[0041] The polish approach of the semiconductor wafer of <polish approach of semiconductor wafer> this invention is the approach of grinding a semiconductor wafer using the aforementioned constituent for polish. although the thing of arbitration can be chosen in combination with abrasives, a scouring pad, and a grinder as a semiconductor wafer -- (**) -- silicon and (**) -- a compound semiconductor, for example, GaAs, and GaP and InP -- and in addition to this, various (Ha) wafers with film, for example, silicon-dioxide film, silicon nitride film, polish recon film, aluminum film, copper film, tungsten film, and other wafer with film ** is mentioned. In this, wafer with film ** of a wafer with the film, especially the silicon-dioxide film is desirable.

[0042] As a grinder used for the polish approach of this invention, the thing of an one side grinder, a double-sided grinder, and other arbitration can be used.

[0043] The following explains concretely the constituent for polish and the polish approach of this invention using an example.

[0044] In addition, this invention is not limited to the configuration of many examples explained below, unless the summary is exceeded.

[0045]

[Embodiment of the Invention]

<the contents of the constituent for polish, and preparation> -- first, water was made to distribute fumed silica (50nm of diameters of a primary particle, 200nm of diameters of an aggregated particle), using an agitator as abrasives, and the slurry of 15 % of the weight of abrasives concentration was prepared. Subsequently, a carbonic acid compound (compound which emits at least one kind chosen from

carbonate ion, the bicarbonate, and the group that consists of carbonic acid), and ammonia (compound which emits ammonium ion) were added, and the sample of examples 1-9 and the examples 1-3 of a comparison was prepared so that it might become the concentration or the content indicated to this slurry in Table 1.

[0046] Here, total carbonic acid concentration expresses with mol concentration the concentration of the carbonic acid compound dissolved in the constituent for polish, and an ammonium ion content expresses with mol concentration the total amount of the ammonium ion dissolved in the constituent for polish. In the example which uses the ammonium salt of carbonic acid as a carbonic acid compound, an ammonium ion content also contains among an example the ammonium ion emitted from the ammonium salt of carbonic acid.

[0047] The polish trial by the sample of <a polish trial> next examples 1-9, and the examples 1-3 of a comparison was performed. As a workpiece, the base of the 6 inch silicon wafer (outer diameter of about 150mm) which formed the silicon-dioxide film with the CVD method was used, and the field with the film of the silicon-dioxide film was ground.

[0048] Polish was performed using the one side grinder (570mm of diameters of a surface plate). The scouring pad which stuck the urethane foam pad (ICmade from Rodel (U.S.)- 1000) on the nonwoven fabric pad (Suba400 made from Rodel (U.S.)) was stuck on the surface plate of a grinder, and it loaded with the wafer with the silicon-dioxide film, and ground for 3 minutes.

[0049] Polish conditions were set to a part for /, and processing pressure force 490 g/cm2, rotating speed 35rpm, and constituent amount-of-supply wafer rotational frequency of 150 cc 70rpm for polish.

[0050] After polish, after sequential-washing the wafer and drying, the polish rate was found according to each trial by measuring 49 decreases of thickness of a wafer, i.e., the machining allowance by polish, averaging it, and **(ing) by polish time amount.

[0051] From the machining allowance of 49 points called for by the above, N-U which is the homogeneous valuation basis of a polished surface was calculated by the degree type.

N-U(%) = -- {-- R. (max) -R.(min)}/-- {-- R. (ave) -- x2} -- in the maximum machining allowance and R. (min), in the x100 top type, the minimum machining allowance and R. (ave) express [R. (max)] the average machining allowance.

[0052] N-U is an index showing the irregularity on the front face of a wafer by dispersion in the decrease of thickness generated in polish, i.e., the heterogeneity of a machining allowance, so that clearly also from this formula. The polished surface where the value of this N-U is larger has larger dispersion in the machining allowance by polish, and the polished surface where the value of N-U is conversely smaller has smaller dispersion in the machining allowance by polish.

[0053]

table 1 Ammonia A carbonic acid compound Carbonic acid compound Polish rate N-U A content Concentration [mol/l] [mol/l] [A part for nm/] [%] Example 1 0.0215 Ammonium carbonate 0.0086 152 4.6 examples 2 0.0347 Ammonium hydrogencarbonate 0.0086 153 6.0 examples 3 0.0347 ammonium carbonates 0.0086 153 6.3 example 4 0.0347 Ammonium carbonate 0.0172 158 6.8 examples 5 0.0614 Ammonium carbonate 0.0086 156 10.0 examples 6 0.0614 ammonium carbonates 0.0172 159 10.1 examples 7 0.0614 Ammonium carbonate 0.0009 149 10.7 example 80.0951 ammonium carbonate 0.086 155 11.5 examples 9 0.1305 ammonium carbonates 0.086 160 Example 1 of 12.7 comparisons 0.0347 - - 124 Example 2 of 6.6 comparisons 0.3071 - - 143 Example 3 of 15.2 comparisons 0.6550 - - 144 19.4 [0054] The conventional constituent for polish has a polish rate remarkably smaller than the result shown in Table 1 as compared with the constituent for polish of this invention, or N-U is remarkably inferior, and it turns out that the constituent for polish of this invention is compatible in the outstanding polish rate and the homogeneity of the outstanding polished surface.

[0055] In addition, although not carried in the above-mentioned table 1, when viewing estimated the ground processing side used by these trials, an example and the example of a comparison were not found out about the surface discontinuity of a scratch and others.

[0056]

[Effect of the Invention] The constituent for polish of this invention has a large polish rate, and it is as

having described above in the term of that the polished surface excellent in homogeneity being made forming and the polish front face on which the polish approach of the semiconductor wafer of this invention was further excellent in the homogeneity in a wafer can be made to be able to form, and the productivity of a semiconductor wafer can be raised, **, and [Summary of the Invention].

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the polish approach of the suitable semiconductor wafer for surface flattening processing of the suitable constituent for polish for surface flattening processing of the device wafer especially in semiconductor industry etc., and a device wafer about the constituent for polish used for polish of various industrial products, such as a semi-conductor, a photo mask, various bases for memory hard disks, and synthetic resin, or the member of those.
[0002] in more detail, in polish of the silicon-dioxide film which is an insulator layer for the interlayer insulation film and isolation to which the CMP technique (detail postscript) is applied conventionally, this invention forms the polish front face excellent in the homogeneity in a wafer at the same time a big polish rate is obtained -- it can make -- the constituent for polish applicable to an advanced device formation technique -- and polish approach Seki is carried out.

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PRIOR ART

[Description of the Prior Art] The so-called advance of high-tech products including a computer in recent years is remarkable, and the components used for this, for example, ULSI, and ****** high integration and improvement in the speed are being enhanced. In connection with this, as for the design rule of a semiconductor device, detailed-ization progresses every year, the depth of focus in a device manufacture process becomes shallow, and the surface smoothness required of a pattern formation side is becoming severe.
[0004] Moreover, although compaction of the wire length by multilayering of a device is performed in order to cope with increase of the wiring resistance by detailed-izing of wiring, the level difference on the formed front face of a pattern has been becoming an issue as a failure of multilayering.
[0005] In performing such detailed-izing and multilayering, it is required in that process to perform flattening on the front face of a request for removing a level difference, and a spin-on glass, resist etchback, and other flattening methods were used as this technique until now.
[0006] However, by such technique, although partial flattening is possible, it is in a difficult situation to attain global pre nari ZESHON (perfect flattening) required of a next-generation device, and flattening (it is called "CMP" Chemical Mechanical Polishing and the following) by mechanical mechanochemical-polishing processing which was, carried out and combined physical polish and chemical polish is examined increasingly current.
[0007] The technical technical problem which hits carrying out flattening of the silicon-dioxide film which is an insulator layer for an interlayer insulation film or isolation using such a polish technique is raising productivity by grinding the field which carries out flattening processing at making homogeneity the neither more nor less and the big polish rate of the machining allowance by polish.
[0008] Conventionally, the constituent for polish containing the basic compound chosen from fumed silica, water and a potassium hydroxide, ammonia, and others has been used for polish of the silicon-dioxide film currently used for the insulator layer for an interlayer insulation film or isolation. When using such a constituent for polish, a polish rate can be enlarged if the quantity of the addition of a basic compound is increased.
[0009] This is because chemical scouring is used in such polish processing. Chemical scouring will mean that the silicon-dioxide film becomes easy to receive removal by polish according to the effectiveness of the basic compound which is a chemical polish accelerator in response to chemical pervasion, if the above-mentioned polish processing is taken for an example. That is, in the above-mentioned polish processing, by increasing the quantity of the addition of a basic compound, a chemical operation increases and the whole polish rate becomes large.

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EFFECT OF THE INVENTION

[Effect of the Invention] The constituent for polish of this invention has a large polish rate, and it is as having described above in the term of that the polished surface excellent in homogeneity being made forming and the polish front face on which the polish approach of the semiconductor wafer of this invention was further excellent in the homogeneity in a wafer can be made to be able to form, and the productivity of a semiconductor wafer can be raised, **, and [Summary of the Invention].

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, although usually comparatively a lot of basic compounds are included and the polish rate of need level was maintained in the conventional constituent for polish which was described above as far as this invention persons get to know, in the homogeneity of a polished surface, it could not be made sufficiently satisfactory level, but there was still room of amelioration. Therefore, establishment of the polish approach of the constituent for polish compatible in sufficient polish rate and the homogeneity of a polished surface and the semiconductor wafer using it was desired.

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MEANS

[Means for Solving the Problem]
[Summary of the Invention]
The constituent for polish of <summary> this invention is at least one kind of cation chosen from the group which consists of at least one kind chosen from (1) water, (2) abrasives, (3) carbonate ion, the bicarbonate, and the group that consists of carbonic acid and (4) ammonium ion, alkali-metal ion, and each alkaline-earth-metal ion. It is the constituent for polish which becomes by ******, and is characterized by the total amount of the cation of (4) being 0.001-0.15 mols/l.
[0012] Moreover, the polish approach of the semiconductor wafer of this invention (1) At least one kind chosen from water, (2) abrasives, (3) carbonate ion, the bicarbonate, and the group that consists of carbonic acid, And are chosen out of the group which consists of (4) ammonium ion, alkali-metal ion, and each alkaline-earth-metal ion. It is the constituent for polish which comes to contain at least one kind of cation, and is characterized by performing surface flattening processing of a semiconductor wafer using the constituent for polish whose total amount of the cation of (4) is 0.001-0.15 mols/l.
[0013] The polished surface the constituent for polish of <effectiveness> this invention had the large polish rate, and homogeneity excelled [polished surface] in coincidence can be made to form.
[0014] Furthermore, the polish approach of the semiconductor wafer of this invention can make the polish front face excellent in the homogeneity in a wafer able to form, and can raise the productivity of a semiconductor wafer.
[0015] [Concrete explanation of invention]
Suitable abrasives to use as abrasives in the constituent for polish of <abrasives> this invention are chosen from a silicon dioxide, an aluminum oxide, cerium oxide, titanium oxide, silicon nitride, a zirconium dioxide, and the group that consists of a manganese dioxide.
[0016] In this invention, it has and that from which the manufacturing method of colloidal silica, fumed silica, and others and description differ recognizes variety existence at the silicon dioxide which can be.
[0017] There are alpha-alumina, delta alumina, theta alumina, kappa alumina, and a different thing like other gestalten also in an aluminum oxide. Moreover, there are some which are called a fumed alumina from a manufacturing method.
[0018] It sees in cerium oxide from a thing trivalent from the oxidation number, a tetravalent thing, and crystal system, and there is a thing of hexagonal system, a tesseral system, and a face-centered cubic system in it.
[0019] It sees in titanium oxide from crystal system, and there is a thing of titanium monoxide, 3 oxidization 2 titanium, a titanium dioxide, and others in it. Moreover, there are some which are called a fumed titania from a manufacturing method.
[0020] Silicon nitride has alpha-silicon nitride, beta-silicon nitride, amorphous silicon nitride, and a different thing like other gestalten.
[0021] A zirconium dioxide is seen from crystal system and has monoclinic system, tetragonal system, and an amorphous thing. Moreover, there are some which are called fumed zirconia from a manufacturing method.

[0022] A manganese dioxide is seen in gestalt and has alpha-manganese dioxide, beta-manganese dioxide, gamma-2 manganese oxide, delta-2 manganese oxide, epsilon-2 manganese oxide, eta-2 manganese oxide, and others.
[0023] These things can be combined and used for the constituent of this invention at arbitration if needed. When combining, especially the how to combine or rate to be used are not limited.
[0024] The above-mentioned abrasives grind a polished surface-ed according to an operation [mechanical / as an abrasive grain]. among these, generally 5-500nm of 10-200nm of particle size of a silicon dioxide comes out preferably with the mean particle diameter called for from the specific surface area measured with the BET adsorption method. moreover, generally an aluminum oxide, a zirconium dioxide, titanium oxide, silicon nitride, and 10-5,000nm of 50-3,000nm of particle size of a manganese dioxide come out preferably with the mean particle diameter called for from the specific surface area measured with the BET adsorption method. furthermore, the particle size of cerium oxide is the mean particle diameter observed by the scanning electron microscope, and, generally comes out 50-3,000nm preferably 10-5,000nm.
[0025] There is a between title of the surface roughness of the ground front face being large when the mean particle diameter of these abrasives is large across the range shown here, or a scratch occurring, and conversely, if smaller than the range shown here, a polish rate becomes extremely small and is not practical.
[0026] the content of the abrasives in the constituent for polish comes out one to 30% of the weight more preferably 0.1 to 40% of the weight on the basis of the weight of a constituent. If remainder has few contents of abrasives, the mechanical operation by abrasives will become weak, a polish rate will become small, when many [to remainder / conversely], it becomes impossible to maintain homogeneity distribution, constituent viscosity may become excessive, and handling may become difficult.
[0027] The constituent for polish of <carbonate ion, bicarbonate, and carbonic acid> this invention comes to contain at least one kind chosen from carbonate ion, the bicarbonate, and the group that consists of carbonic acid. As for carbonate ion and the bicarbonate, it is [among these] common to make it generate in the constituent for polish by dissolving the carbonic acid compound which dissolves in water and emits carbonate ion or the bicarbonate, i.e., carbonic acid, and its salt. Moreover, in this invention, since a main solvent is water, if a carbon dioxide is directly introduced into water, carbonic acid and the above-mentioned ion will generate.
[0028] The thing of arbitration can be used for the carbonic acid compound to be used if effectiveness of this invention is not spoiled. It is desirable that it is at least one kind of compound specifically chosen from the group which consists of potassium carbonate, an ammonium carbonate, a sodium carbonate, potassium sodium carbonate, a lithium carbonate, carbonic acid beryllium, a magnesium carbonate, a calcium carbonate, a potassium hydrogencarbonate, an ammonium hydrogencarbonate, a sodium hydrogencarbonate, and a carbonic acid hydrogen lithium. When a metal ion takes into consideration in these the effect and others which are given to a semiconductor device, especially ammonium-carbonate, ammonium-hydrogencarbonate, potassium carbonate, and potassium-hydrogencarbonate ** is desirable. Moreover, since an unnecessary metal ion is not introduced into the constituent for polish, it is also desirable to use a carbon dioxide. The salt (or carbon dioxide) of these carbonic acid can also be used together at a rate of arbitration.
[0029] In the constituent for polish of this invention, although the concentration of the total carbonic acid which are carbonate ion, the bicarbonate, and the total amount of carbonic acid is not limited unless the effectiveness of this invention is spoiled, it is desirable that the concentration of a total carbonic acid is 1/2 in a mole ratio to the total amount of the below-mentioned cation as a relative amount with the cation mentioned later, and it is desirable that it is especially 1/1. [200-2] [100-1] Although it is in the inclination for a polish rate to become large by making concentration of a total carbonic acid high, since the dispersibility of abrasives may get worse when it increases too much, cautions are required.
[0030] Although it is more desirable to the constituent for polish of this invention to introduce carbonate ion or the bicarbonate into the constituent for polish by using a water-soluble (soluble) carbonic acid compound from points, such as handling nature, it is possible to use, if dissolving into the constituent for

polish is possible even if it is a poorly soluble compound. In other words, the ratios of the concentration of the aforementioned total carbonic acid and the total amount of a cation are the carbonate ion which is dissolving, the bicarbonate, and an amount based on carbonic acid, and it is not necessary to take into consideration the carbonic acid compound which exists in a constituent with a solid-state, without having dissolved by having added the amount more than the solubility of the compound. Moreover, as for an insoluble carbonic acid compound, it is desirable to remove, since it may become the cause of the surface discontinuity of a scratch or others.

[0031] The constituent for polish of <cation> this invention comes to contain a specific cation. In the constituent for polish of this invention, when used, these cations are the aforementioned carbonate ion, the bicarbonate, carbonic acid, or independent, and promote scouring according to an operation [KEMIKARU / as a polish accelerator].

[0032] The cation used in this invention is at least one kind of cation chosen from the group which consists of ammonium ion, alkali-metal ion, and each alkaline-earth-metal ion. The ion (henceforth "inorganic alkali ion") chosen from the group which consists of NH4+, Li+, Na+, K+, Be2+, Mg2+, and calcium2+ among these cations is desirable, and when the effect which it has on a vice with a semi-conductor is taken into consideration, NH4+ and especially K+ are desirable. Such ion is introduced into the constituent for polish by usually dissolving the basic compound which emits the aforementioned inorganic alkali ion into the constituent for polish. Although it will not be limited especially if the basic compound used here does not spoil the effectiveness of this invention, at least one kind of compound specifically chosen from the group which consists of a potassium hydroxide, ammonium hydroxide, a sodium hydroxide, a lithium hydroxide, hydroxylation beryllium, a magnesium hydroxide, and a calcium hydroxide is mentioned. These basic compounds can also be used together at a rate of arbitration. Moreover, about the above-mentioned basic compound, when metal ions other than the aforementioned inorganic alkali ion use the thing of very few high grades, since an impurity metal ion can be decreased in the constituent for polish, it is desirable.

[0033] although the content of the aforementioned inorganic alkali ion of the constituent for polish of this invention changes with classes of basic compound to be used -- the whole quantity of the constituent for polish -- receiving -- 0.001-0.15 mols/l. -- 0.01-0.075 mols [/] 0.005-0.1 mols /come out l. more preferably l. Although there is an inclination for a polish rate to become large by increasing the quantity of the content of said inorganic alkali ion, when many, it is in the inclination for the homogeneity of a polished surface to get worse. Furthermore, since the degree of amelioration to a polish rate etc. becomes small and may produce an economical demerit, cautions are required.

[0034] The constituent for polish of <constituent for polish> this invention makes water mix and distribute the above-mentioned abrasives with desired content generally, and is prepared by carrying out the specified quantity dissolution of carbonate ion, the bicarbonate, the compound that emits at least one kind chosen from carbonic acid, and the compound which emits the aforementioned inorganic alkali ion further. The method of distributing or dissolving these components underwater is arbitrary, for example, it agitates with a wing formula agitator, or it is distributed by ultrasonic distribution. Moreover, the mixed sequence foreword of each of these components is arbitrary, and may perform first whichever of the dissolution of distribution of abrasives, and a carbonic acid compound or a basic compound, and may perform both to coincidence.

[0035] Moreover, on the occasion of preparation of the constituent for polish of this invention, various kinds of well-known additives may be added further the purpose which attains quality maintenance and stabilization of a product, the class of workpiece, processing conditions, and if needed on other polish processings.

[0036] That is, the following are mentioned as a suitable example of the additive added further.

(b) Celluloses, for example, a cellulose, a carboxymethyl cellulose, Hydroxyethyl cellulose and others, (b) water solubility alcohols, For example, ethanol, propanol, ethylene glycol, and others, A surface active agent, for example, alkylbenzene-sulfonic-acid soda, the formalin condensate of naphthalenesulfonic acid, (Ha) and -- in addition to this -- (**) -- the organic poly anion system matter, for example, a ligninsulfonic acid salt, and polyacrylate -- and -- in addition to this -- (**) -- water

soluble polymers (emulsifier), for example, polyvinyl alcohol, -- and -- in addition to this -- a (**) germicide, for example, sodium alginate, -- and -- in addition to this .

[0037] Moreover, although a thing is included said bottom as abrasives, a carbonic acid compound, and a basic compound in addition to the abrasives contained to the constituent for polish of this invention there, a carbonic acid compound, and a basic compound, it is also possible to be the purposes other than the application of abrasives or a polish accelerator, for example, to use the thing of inside to others as further additive for sedimentation prevention of abrasives.

[0038] it usually comes out of the constituent for polish of this invention that pH is set to 4-10 by said addition of a principal component carried out. Although pH of the constituent for polish is changed by addition of various kinds of auxiliary additives, in order to make the effectiveness of this invention discover, it is desirable that pH is 4-10. Therefore, when pH of the constituent for polish shifts from the range of 4-10, it is desirable to add an acid or alkali and to adjust pH. Moreover, even if pH is within the limits of this, it is [other being reasons, for example, the preservation stability of the constituent for polish, being / of a polish object / the physical properties, and] sometimes desirable for it to be alike and to adjust pH more nearly further in addition to this.

[0039] In addition, although the constituent for polish of this invention can be applied to the base material of arbitration, such as various industrial products, such as a semi-conductor, a photo mask, various bases for memory hard disks, and synthetic resin, or a member of those, it is desirable to use for surface flattening processing of the device wafer especially in semiconductor industry etc.

[0040] Moreover, the constituent for polish of this invention can be prepared as a comparatively high-concentration undiluted solution, can carry out storage or transportation, and it can also be diluted and used for it at the time of actual polish processing. When the above-mentioned desirable density range was indicated as a thing at the time of actual polish processing and it takes such operation, it cannot be overemphasized that it becomes a more high-concentration solution in the condition of carrying out storage or transportation. Moreover, it is desirable to be manufactured with such a condensed gestalt from a viewpoint of handling nature. In addition, the concentration mentioned above indicates not the concentration at the time of such manufacture but the concentration at the time of use about the constituent for polish.

[0041] The polish approach of the semiconductor wafer of <polish approach of semiconductor wafer> this invention is the approach of grinding a semiconductor wafer using the aforementioned constituent for polish. although the thing of arbitration can be chosen in combination with abrasives, a scouring pad, and a grinder as a semiconductor wafer -- (**) -- silicon and (**) -- a compound semiconductor, for example, GaAs, and GaP and InP -- and in addition to this, various (Ha) wafers with film, for example, silicon-dioxide film, silicon nitride film, polish recon film, aluminum film, copper film, tungsten film, and other wafer with film ** is mentioned. In this, wafer with film ** of a wafer with the film, especially the silicon-dioxide film is desirable.

[0042] As a grinder used for the polish approach of this invention, the thing of an one side grinder, a double-sided grinder, and other arbitration can be used.

[0043] The following explains concretely the constituent for polish and the polish approach of this invention using an example.

[0044] In addition, this invention is not limited to the configuration of many examples explained below, unless the summary is exceeded.

[0045]

[Embodiment of the Invention]

<the contents of the constituent for polish, and preparation> -- first, water was made to distribute fumed silica (50nm of diameters of a primary particle, 200nm of diameters of an aggregated particle), using an agitator as abrasives, and the slurry of 15 % of the weight of abrasives concentration was prepared. Subsequently, a carbonic acid compound (compound which emits at least one kind chosen from carbonate ion, the bicarbonate, and the group that consists of carbonic acid), and ammonia (compound which emits ammonium ion) were added, and the sample of examples 1-9 and the examples 1-3 of a comparison was prepared so that it might become the concentration or the content indicated to this slurry

in Table 1.
[0046] Here, total carbonic acid concentration expresses with mol concentration the concentration of the carbonic acid compound dissolved in the constituent for polish, and an ammonium ion content expresses with mol concentration the total amount of the ammonium ion dissolved in the constituent for polish. In the example which uses the ammonium salt of carbonic acid as a carbonic acid compound, an ammonium ion content also contains among an example the ammonium ion emitted from the ammonium salt of carbonic acid.
[0047] The polish trial by the sample of <a polish trial> next examples 1-9, and the examples 1-3 of a comparison was performed. As a workpiece, the base of the 6 inch silicon wafer (outer diameter of about 150mm) which formed the silicon-dioxide film with the CVD method was used, and the field with the film of the silicon-dioxide film was ground.
[0048] Polish was performed using the one side grinder (570mm of diameters of a surface plate). The scouring pad which stuck the urethane foam pad (ICmade from Rodel (U.S.)- 1000) on the nonwoven fabric pad (Suba400 made from Rodel (U.S.)) was stuck on the surface plate of a grinder, and it loaded with the wafer with the silicon-dioxide film, and ground for 3 minutes.
[0049] Polish conditions were set to a part for /, and processing pressure force 490 g/cm2, rotating speed 35rpm, and constituent amount-of-supply wafer rotational frequency of 150 cc 70rpm for polish.
[0050] After polish, after sequential-washing the wafer and drying, the polish rate was found according to each trial by measuring 49 decreases of thickness of a wafer, i.e., the machining allowance by polish, averaging it, and **(ing) by polish time amount.
[0051] From the machining allowance of 49 points called for by the above, N-U which is the homogeneous valuation basis of a polished surface was calculated by the degree type.
N-U(%) = -- {-- R. (max) -R.(min)}/-- {-- R. (ave) -- x2} -- in the maximum machining allowance and R. (min), in the x100 top type, the minimum machining allowance and R. (ave) express [R. (max)] the average machining allowance.
[0052] N-U is an index showing the irregularity on the front face of a wafer by dispersion in the decrease of thickness generated in polish, i.e., the heterogeneity of a machining allowance, so that clearly also from this formula. The polished surface where the value of this N-U is larger has larger dispersion in the machining allowance by polish, and the polished surface where the value of N-U is conversely smaller has smaller dispersion in the machining allowance by polish.
[0053]
table 1 Ammonia A carbonic acid compound Carbonic acid compound Polish rate N-U A content Concentration [mol/l] [mol/l] [A part for nm/] [%] Example 1 0.0215 Ammonium carbonate 0.0086 152 4.6 examples 2 0.0347 Ammonium hydrogencarbonate 0.0086 153 6.0 examples 3 0.0347 ammonium carbonates 0.0086 153 6.3 example 4 0.0347 Ammonium carbonate 0.0172 158 6.8 examples 5 0.0614 Ammonium carbonate 0.0086 156 10.0 examples 6 0.0614 ammonium carbonates 0.0172 159 10.1 examples 7 0.0614 Ammonium carbonate 0.0009 149 10.7 example 80.0951 ammonium carbonate 0.086 155 11.5 examples 9 0.1305 ammonium carbonates 0.086 160 Example 1 of 12.7 comparisons 0.0347 - - 124 Example 2 of 6.6 comparisons 0.3071 - - 143 Example 3 of 15.2 comparisons 0.6550 - - 144 19.4 [0054] The conventional constituent for polish has a polish rate remarkably smaller than the result shown in Table 1 as compared with the constituent for polish of this invention, or N-U is remarkably inferior, and it turns out that the constituent for polish of this invention is compatible in the outstanding polish rate and the homogeneity of the outstanding polished surface.
[0055] In addition, although not carried in the above-mentioned table 1, when viewing estimated the ground processing side used by these trials, an example and the example of a comparison were not found out about the surface discontinuity of a scratch and others.

[Translation done.]

L1: Entry 4 of 4 File: DWPI Mar 26, 1999

DERWENT-ACC-NO: 1999-267436
DERWENT-WEEK: 199923

TITLE: Grinding composition - consisting of water, grinding agent, carbonic acid ions, ammonium ions, and alkaline(earth) metal ions

PRIORITY-DATA: 1997JP-0244331 (September 9, 1997)

Search Selected | Search ALL | Clear

PATENT-FAMILY:

	PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
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INT-CL (IPC): B24 B 37/00; C09 K 3/14; G11 B 5/84; H01 L 21/304

ABSTRACTED-PUB-NO: JP 11080707A
BASIC-ABSTRACT:

Grinding composition, comprises (1) water, (2) grinding agent, (3) carbonic acid ion, or hydrocarbonic acid ion, and (4) ammonium ion, alkaline metal ion or alkaline earth metal ion in an amount of 0.001 to 0.15 mole/liter.

ADVANTAGE - Grinding at high speed can be conducted to give homogeneous ground surface.

PUB-NO: JP411080707A
DOCUMENT-IDENTIFIER: JP 11080707 A
TITLE: POLISHING AND COMPOSITION THEREFOR

PUBN-DATE: March 26, 1999

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INT-CL (IPC): C09 K 3/14; B24 B 37/00; H01 L 21/304; G11 B 5/84

ABSTRACT:

PROBLEM TO BE SOLVED: To obtain a composition for polishing, having a high polishing rate and capable of forming a polished surface excellent in uniformity and to provide a method for polishing a semiconductor wafer having high productivity.

SOLUTION: This composition for polishing comprises (1) water, (2) a polishing material, (3) at least one selected from the group consisting of carbonate ions, hydrogencarbonate ions and carbonic acid and (4) at least one cation selected from the group consisting of ammonium ions, alkali metallic ions and alkaline earth metallic ions. In this case, the total amount of the cation (4) is 0.001-0.15 mol/L. The method for polishing a semiconductor wafer comprises carrying out the surface flattening working of the semiconductor wafer with the composition for polishing.

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TI **Polishing** compositions and **polishing** of **semiconductor wafer**
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	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PRAI	JP 1997-244331		19970909		

AB The **polishing** compns. contain (1) water, (2) 0.1-40 wt.% abrasives, (3) ≥1 of CO_3^{2-}, HCO_3^-, and H_2CO_3, and (4) ≥1 of NH_4^+, alkali metal ion, and alk. earth metal ion at 0.001-0.15 mol/L. The abrasives are selected from SiO_2, Al_2O_3, CeO_2, TiO_2, Si_3N_4, ZrO_2, and/or MnO_2. The surface flattening of **semiconductor wafers** is carried out by using the **polishing** compns.

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最終頁に続く

(54)【発明の名称】　研磨用組成物および研磨方法

(57)【要約】
【課題】　研磨速度が大きく、均一性が優れた研磨面を形成させることができる研磨用組成物、および生産性の高い半導体ウェーハの研磨方法の提供。
【解決手段】　（１）水、（２）研磨材、（３）炭酸イオン、炭酸水素イオン、および炭酸からなる群より選ばれる少なくとも１種類、ならびに（４）アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンそれぞれからなる群から選ばれる、少なくとも１種類の陽イオン、を含んでなる研磨用組成物であって、（４）の陽イオンの総量が０．００１～０．１５モル／リットルであることを特徴とする研磨用組成物、およびその研磨用組成物を用いた半導体ウェーハの研磨方法。

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【特許請求の範囲】

【請求項1】（1）水、（2）研磨材、（3）炭酸イオン、炭酸水素イオン、および炭酸からなる群より選ばれる少なくとも1種類、ならびに（4）アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンそれぞれからなる群から選ばれる、少なくとも1種類の陽イオン、を含んでなる研磨用組成物であって、

（4）の陽イオンの総量が0．001～0．15モル／リットルであることを特徴とする研磨用組成物。

【請求項2】研磨材が、二酸化ケイ素、酸化アルミニウム、酸化セリウム、酸化チタン、窒化ケイ素、酸化ジルコニウム、および二酸化マンガンからなる群より選ばれる少なくとも1種類の研磨材である、請求項1に記載の研磨用組成物。

【請求項3】研磨材の含有量が、研磨用組成物の重量を基準にして、0．1～40重量%である請求項1または2のいずれかに記載の研磨用組成物。

【請求項4】陽イオンが、NH_4^+、Li^+、Na^+、K^+、Be^{2+}、Mg^{2+}、およびCa^{2+}からなる群より選ばれる少なくとも1種類の陽イオンである、請求項1～3のいずれか1項に記載の研磨用組成物。

【請求項5】陽イオンの総量が、0．005～0．1モル／リットルである、請求項1～4のいずれか1項に記載の研磨用組成物。

【請求項6】陽イオンの総量が、0．01～0．075モル／リットルである、請求項1～4のいずれか1項に記載の研磨用組成物。

【請求項7】炭酸イオン、炭酸水素イオン、および炭酸からなる全炭酸の総量が、前記陽イオンに対して、モル比で1／200～2である、請求項1～6のいずれか1項に記載の研磨用組成物。

【請求項8】（1）水、（2）研磨材、（3）炭酸イオン、炭酸水素イオン、および炭酸からなる群より選ばれる少なくとも1種類、ならびに（4）アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンそれぞれからなる群から選ばれる、少なくとも1種類の陽イオン、を含んでなる研磨用組成物であって、

（4）の陽イオンの総量が0．001～0．15モル／リットルである研磨用組成物を用いて、半導体ウェーハの表面平坦化加工を行うことを特徴とする、半導体ウェーハの研磨方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、半導体、フォトマスク、各種メモリーハードディスク用基盤および合成樹脂等各種工業製品またはその部材の研磨に使用される研磨用組成物に関し、特に半導体産業等におけるデバイスウェーハの表面平坦化加工に好適な研磨用組成物、およびデバイスウェーハの表面平坦化加工に好適な半導体ウェーハの研磨方法に関するものである。

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【0002】さらに詳しくは、本発明は、従来よりCMP技術（詳細後記）が適用されている、層間絶縁膜および素子分離のための絶縁膜である二酸化ケイ素膜の研磨において、大きな研磨速度が得られると同時に、ウェーハ内の均一性が優れた研磨表面を形成させることができ、高度なデバイス形成技術に適用可能な研磨用組成物におよび研磨方法関するものである。

【0003】

【従来の技術】近年のコンピューターを始めとする所謂ハイテク製品の進歩は目覚ましく、これに使用される部品、例えばULSI、は年々高集積化・高速化の一途をたどっている。これに伴い、半導体装置のデザインルールは年々微細化が進み、デバイス製造プロセスでの焦点深度は浅くなり、パターン形成面に要求される平坦性は厳しくなってきている。

【0004】また、配線の微細化による配線抵抗の増大に対処するため、デバイスの多層化による配線長の短縮が行われているが、形成されたパターン表面の段差が多層化の障害として問題化してきている。

【0005】このような微細化および多層化を行うに当たっては、そのプロセス中で段差を取り除くための所望表面の平坦化を行うことが必要であり、この手法として、これまではスピンオングラス、レジストエッチバックおよびその他の平坦化法が用いられていた。

【0006】しかし、これらの手法では、部分的な平坦化は可能であるが、次世代のデバイスに要求されるグローバルプレナリゼーション（完全平坦化）を達成することは困難な状況であり、現在では機械的ないし物理的研磨と化学的研磨とを組み合わせたメカノケミカル研磨加工による平坦化（Chemical Mechanical Polishing、以下「CMP」という）が検討されるようになってきている。

【0007】このような研磨技術を用いて、層間絶縁膜または素子分離のための絶縁膜である二酸化ケイ素膜の平坦化を実施するに当たっての技術課題は、平坦化加工する面を研磨による取代の過不足なく均一に仕上げること、および大きな研磨速度で研磨することにより生産性を向上させることである。

【0008】従来、層間絶縁膜または素子分離のための絶縁膜に使用されている二酸化ケイ素膜の研磨には、フュームドシリカ、水、および水酸化カリウム、アンモニアおよびその他から選ばれた塩基性化合物を含む研磨用組成物が用いられてきた。このような研磨用組成物を用いる場合、塩基性化合物の添加量を増量すると研磨速度を大きくすることができる。

【0009】これは、このような研磨加工において、化学的な研磨作用が利用されているためである。化学的な研磨作用とは、上記の研磨加工を例にとれば、二酸化ケイ素膜が、化学的研磨促進剤である塩基性化合物の効果により化学的な侵食を受けて、研磨による除去を受けや

すくなることをいう。すなわち、上記の研磨加工において、塩基性化合物の添加量を増量することにより化学的な作用が増大して、全体の研磨速度が大きくなるのである。

【００１０】

【発明が解決しようとする課題】しかしながら、本発明者らの知る限り、上記したような従来の研磨用組成物においては、通常、比較的多量の塩基性化合物を含んでおり、必要レベルの研磨速度は維持されているものの、研磨面の均一性においては十分満足なレベルにすることができず、まだ改良の余地があった。従って、十分な研磨速度と、研磨面の均一性とを両立できる研磨用組成物、およびそれを用いた半導体ウェーハの研磨方法の確立が望まれていた。

【００１１】

【課題を解決するための手段】

［発明の概要］

＜要旨＞本発明の研磨用組成物は、（１）水、（２）研磨材、（３）炭酸イオン、炭酸水素イオン、および炭酸からなる群より選ばれる少なくとも１種類、ならびに（４）アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンそれぞれからなる群から選ばれる、少なくとも１種類の陽イオン。を含んでなる研磨用組成物であって、（４）の陽イオンの総量が０．００１～０．１５モル／リットルであること、を特徴とするものである。

【００１２】また、本発明の半導体ウェーハの研磨方法は、（１）水、（２）研磨材、（３）炭酸イオン、炭酸水素イオン、および炭酸からなる群より選ばれる少なくとも１種類、ならびに（４）アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンそれぞれからなる群から選ばれる、少なくとも１種類の陽イオン、を含んでなる研磨用組成物であって、（４）の陽イオンの総量が０．００１～０．１５モル／リットルである研磨用組成物を用いて、半導体ウェーハの表面平坦化加工を行うこと、を特徴とするものである。

【００１３】＜効果＞本発明の研磨用組成物は、研磨速度が大きく、同時に均一性が優れた研磨面を形成させることができる。

【００１４】さらに、本発明の半導体ウェーハの研磨方法は、ウェーハ内の均一性が優れた研磨表面を形成させることができて、半導体ウェーハの生産性を向上させることができる。

【００１５】［発明の具体的説明］

＜研磨材＞本発明の研磨用組成物において研磨材として用いるのに適当な研磨材は、二酸化ケイ素、酸化アルミニウム、酸化セリウム、酸化チタン、窒化ケイ素、酸化ジルコニウム、および二酸化マンガンからなる群から選ばれるものである。

【００１６】本発明において、もちいることのできる二酸化ケイ素には、コロイダルシリカ、フュームドシリカ、およびその他の、製造法や性状の異なるものが多種存在する。

【００１７】酸化アルミニウムにも、α－アルミナ、δ－アルミナ、θ－アルミナ、κ－アルミナ、およびその他の形態的に異なるものがある。また製造法からフュームドアルミナと呼ばれるものもある。

【００１８】酸化セリウムには、酸化数から３価のものと４価のもの、また結晶系から見て、六方晶系、等軸晶系、および面心立方晶系のものがある。

【００１９】酸化チタンには、結晶系から見て、一酸化チタン、三酸化二チタン、二酸化チタンおよびその他のものがある。また製造法からフュームドチタニアと呼ばれるものもある。

【００２０】窒化ケイ素は、α－窒化ケイ素、β－窒化ケイ素、アモルファス窒化ケイ素、およびその他の形態的に異なるものがある。

【００２１】酸化ジルコニウムは、結晶系から見て、単斜晶系、正方晶系、および非晶質のものがある。また、製造法からフュームドジルコニアと呼ばれるものもある。

【００２２】二酸化マンガンは、形態的に見てα－二酸化マンガン、β－二酸化マンガン、γ－二酸化マンガン、δ－二酸化マンガン、ε－二酸化マンガン、η－二酸化マンガン、およびその他がある。

【００２３】本発明の組成物には、これらのものを任意に、必要に応じて組み合わせて、用いることができる。組み合わせる場合には、その組み合わせ方や使用する割合は特に限定されない。

【００２４】上記の研磨材は、砥粒としてメカニカルな作用により被研磨面を研磨するものである。このうち二酸化ケイ素の粒径は、ＢＥＴ法により測定した比表面積から求められる平均粒子径で一般に５～５００ｎｍ、好ましくは１０～２００ｎｍ、である。また、酸化アルミニウム、酸化ジルコニウム、酸化チタン、窒化ケイ素、および二酸化マンガンの粒径は、ＢＥＴ法により測定した比表面積から求められる平均粒子径で一般に１０～５，０００ｎｍ、好ましくは５０～３，０００ｎｍ、である。さらに、酸化セリウムの粒径は、走査型電子顕微鏡により観察される平均粒子径で、一般に１０～５，０００ｎｍ、好ましくは５０～３，０００ｎｍ、である。

【００２５】これらの研磨材の平均粒子径がここに示した範囲を超えて大きいと、研磨された表面の表面粗さが大きかったり、スクラッチが発生したりするなどの問題があり、逆に、ここに示した範囲よりも小さいと研磨速度が極端に小さくなってしまい実用的でない。

【００２６】研磨用組成物中の研磨材の含有量は、組成物の重量を基準にして、好ましくは０．１～４０重量％、より好ましくは１～３０重量％、である。研磨材の含有量が余りに少ないと、研磨材によるメカニカルな作

用が弱くなり研磨速度が小さくなり、逆に余りに多いと均一分散が保てなくなり、かつ組成物粘度が過大となって取扱いが困難となることがある。

【００２７】＜炭酸イオン、炭酸水素イオン、炭酸＞本発明の研磨用組成物は、炭酸イオン、炭酸水素イオン、および炭酸からなる群より選ばれる少なくとも１種類を含んでなる。これらのうち、炭酸イオンおよび炭酸水素イオンは、水に溶解して炭酸イオンまたは炭酸水素イオンを放出する炭酸化合物、すなわち、炭酸、またはその塩、を溶解することにより研磨用組成物中に生成させるのが普通である。また、本発明において、主たる溶媒は水であるので、二酸化炭素を水に直接導入すると炭酸および上記のイオンが生成する。

【００２８】用いる炭酸化合物は、本発明の効果を損なわないものであれば任意のものを用いることができる。具体的には、炭酸カリウム、炭酸アンモニウム、炭酸ナトリウム、炭酸カリウムナトリウム、炭酸リチウム、炭酸ベリリウム、炭酸マグネシウム、炭酸カルシウム、炭酸水素カリウム、炭酸水素アンモニウム、炭酸水素ナトリウム、および炭酸水素リチウムからなる群から選ばれる少なくとも１種類の化合物であることが好ましい。これらの中で、金属イオンが半導体デバイスに与える影響およびその他を考慮すると、炭酸アンモニウム、炭酸水素アンモニウム、炭酸カリウム、および炭酸水素カリウム、が特に好ましい。また、不必要な金属イオンを研磨用組成物中に導入しないので、二酸化炭素を用いることも好ましい。これらの炭酸の塩（または二酸化炭素）は任意の割合で併用することもできる。

【００２９】本発明の研磨用組成物において、炭酸イオン、炭酸水素イオン、および炭酸の合量である全炭酸の濃度は、本発明の効果を損なわない限り限定されないが、後述する陽イオンとの相対量として、全炭酸の濃度が、後述の陽イオンの総量に対して、モル比で１／２００～２であることが好ましく、１／１００～１であることが特に好ましい。全炭酸の濃度を高くすることで研磨速度が大きくなる傾向にあるが、過度に増量すると研磨材の分散性が悪化することもあるので注意が必要である。

【００３０】本発明の研磨用組成物には、取り扱い性などの点から、水溶性（易溶性）の炭酸化合物を用いることにより、研磨用組成物に炭酸イオンまたは炭酸水素イオンを導入することがより好ましいが、難溶性の化合物であっても研磨用組成物中に溶解することが可能なものであれば用いることが可能である。言い換えれば、前記の全炭酸の濃度と陽イオンの総量の比率は、溶解している炭酸イオン、炭酸水素イオン、および炭酸をもとにした量であり、その化合物の溶解度以上の量を添加されたことにより溶解しきらずに固体のまま組成物中に存在する炭酸化合物は考慮する必要がない。また、溶解していない炭酸化合物は、スクラッチまたはその他の表面欠陥

の原因となる場合があるので除去することが好ましい。

【００３１】＜陽イオン＞本発明の研磨用組成物は、特定の陽イオンを含んでなる。本発明の研磨用組成物において、これらの陽イオンは、用いられる場合には、前記の炭酸イオン、炭酸水素イオン、または炭酸とともに、または単独で、研磨促進剤としてケミカルな作用により研磨作用を促進するものである。

【００３２】本発明において用いられる陽イオンは、アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンそれぞれからなる群から選ばれる、少なくとも１種類の陽イオンである。これらの陽イオンの内、NH_4^+、Li^+、Na^+、K^+、Be^{2+}、Mg^{2+}、およびCa^{2+}からなる群から選ばれるイオン（以下、「無機アルカリイオン」という）が好ましく、半導体でバイスに与える影響を考慮すると、NH_4^+、K^+が特に好ましい。このようなイオンは、通常、前記の無機アルカリイオンを放出する塩基性化合物を研磨用組成物中に溶解させることにより、研磨用組成物中に導入される。ここで用いられる塩基性化合物は、本発明の効果を損なわないものであれば特に限定されないが、具体的には、水酸化カリウム、水酸化アンモニウム、水酸化ナトリウム、水酸化リチウム、水酸化ベリリウム、水酸化マグネシウム、および水酸化カルシウムからなる群から選ばれる少なくとも１種類の化合物が挙げられる。これらの塩基性化合物は任意の割合で併用することもできる。また、上記の塩基性化合物については、前記の無機アルカリイオン以外の金属イオンが極めて少ない高純度のものを使用することにより、研磨用組成物中に不純物金属イオンを減少させることができるので好ましい。

【００３３】本発明の研磨用組成物の前記の無機アルカリイオンの含有量は、用いる塩基性化合物の種類により異なるが、研磨用組成物の全量に対して、０．００１～０．１５モル／リットル、好ましくは０．００５～０．１モル／リットル、より好ましくは、０．０１～０．０７５モル／リットル、である。前記無機アルカリイオンの含有量を増量することで研磨速度が大きくなる傾向があるが、多いと研磨面の均一性が悪化する傾向にある。さらには、研磨速度などに対する改良の度合いが小さくなり、経済的なデメリットを生じることもあり得るので注意が必要である。

【００３４】＜研磨用組成物＞本発明の研磨用組成物は、一般に上記の研磨材を所望の含有率で水に混合し、分散させ、さらに炭酸イオン、炭酸水素イオン、および炭酸から選ばれる少なくとも１種類を放出する化合物、および前記の無機アルカリイオンを放出する化合物を所定量溶解させることにより調製する。これらの成分を水中に分散または溶解させる方法は任意であり、例えば、翼式撹拌機で撹拌したり、超音波分散により分散させる。また、これらの各成分の混合順序は任意であり、研磨材の分散と、炭酸化合物または塩基性化合物の溶解の

どちらを先に行ってもよく、また両者を同時に行ってもよい。

【００３５】また、本発明の研磨用組成物の調製に際しては、製品の品質保持や安定化を図る目的や、被加工物の種類、加工条件およびその他の研磨加工上の必要に応じて、各種の公知の添加剤をさらに加えてもよい。

【００３６】すなわち、さらに加える添加剤の好適な例としては、下記のものが挙げられる。

（イ）セルロース類、例えばセルロース、カルボキシメチルセルロース、ヒドロキシエチルセルロース、およびその他、（ロ）水溶性アルコール類、例えばエタノール、プロパノール、エチレングリコール、およびその他、（ハ）界面活性剤、例えばアルキルベンゼンスルホン酸ソーダ、ナフタリンスルホン酸のホルマリン縮合物、およびその他、（ニ）有機ポリアニオン系物質、例えばリグニンスルホン酸塩、ポリアクリル酸塩、およびその他、（ホ）水溶性高分子（乳化剤）類、例えばポリビニルアルコール、およびその他、（ヘ）殺菌剤、例えばアルギン酸ナトリウム、およびその他。

【００３７】また、本発明の研磨用組成物に対して、そこに含まれる研磨材、炭酸化合物、および塩基性化合物に加えて、研磨材、炭酸化合物、および塩基性化合物として前記したものを包含するものの中からその他のものを、研磨材または研磨促進剤の用途以外の目的で、例えば研磨材の沈降防止のために、さらなる添加剤として用いることも可能である。

【００３８】本発明の研磨用組成物は、前記した主成分の添加により、ｐＨが４～１０となるのが普通である。各種の補助添加剤の添加により研磨用組成物のｐＨは変動するが、本発明の効果を発現させるためにはｐＨが４～１０であることが好ましい。従って、研磨用組成物のｐＨが４～１０の範囲からはずれてしまう場合、酸またはアルカリを添加してｐＨを調整することが好ましい。また、ｐＨがこの範囲内にあっても、その他の理由、例えば研磨用組成物の保存安定性、研磨対象物の物性、およびその他、によりさらにｐＨを調整することが好ましいこともある。

【００３９】なお、本発明の研磨用組成物は、半導体、フォトマスク、各種メモリーハードディスク用基盤および合成樹脂等各種工業製品またはその部材などの任意の基材に対して適用することが可能であるが、特に半導体産業等におけるデバイスウェーハの表面平坦化加工に用いることが好ましい。

【００４０】また、本発明の研磨用組成物は、比較的高濃度の原液として調製して貯蔵または輸送などをし、実際の研磨加工時に希釈して使用することもできる。前述の好ましい濃度範囲は、実際の研磨加工時のものとして記載したのであり、このような使用方法をとる場合、貯蔵または輸送などをされる状態においてはより高濃度の溶液となることは言うまでもない。また、取り扱い性の観点から、そのような濃縮された形態で製造されることが好ましい。なお、研磨用組成物について前述した濃度などは、このような製造時の濃度ではなく、使用時の濃度を記載したものである。

【００４１】＜半導体ウェーハの研磨方法＞本発明の半導体ウェーハの研磨方法は、前記の研磨用組成物を用いて半導体ウェーハを研磨する方法である。半導体ウェーハとしては、研磨材、研磨パッドおよび研磨機との組合せで任意のものを選択することができるが、例えば（イ）シリコン、（ロ）化合物半導体、例えばＧａＡｓ、ＧａＰ、ＩｎＰ、およびその他、（ハ）各種膜付ウェーハ、例えば二酸化ケイ素膜、窒化ケイ素膜、ポリシリコン膜、アルミニウム膜、銅膜、タングステン膜、およびその他の膜付ウェーハ、が挙げられる。この中で、膜付ウェーハ、特に二酸化ケイ素膜の膜付ウェーハ、が好ましい。

【００４２】本発明の研磨方法に用いる研磨機としては、片面研磨機、両面研磨機、およびその他の任意のものを用いることができる。

【００４３】以下は、本発明の研磨用組成物、および研磨方法を例を用いて具体的に説明するものである。

【００４４】なお、本発明は、その要旨を超えない限り、以下に説明する諸例の構成に限定されない。

【００４５】

【発明の実施の形態】

＜研磨用組成物の内容および調製＞まず、研磨材としてフュームドシリカ（一次粒子径５０ｎｍ、二次粒子径２００ｎｍ）を撹拌機を用いて水に分散させて、研磨材濃度１５重量％のスラリーを調製した。次いでこのスラリーに表１に記載した濃度または含有量となるように炭酸化合物（炭酸イオン、炭酸水素イオン、および炭酸からなる群より選ばれる少なくとも１種類を放出する化合物）およびアンモニア（アンモニウムイオンを放出する化合物）を添加して実施例１～９および比較例１～３の試料を調製した。

【００４６】ここで、全炭酸濃度とは、研磨用組成物中に溶存している炭酸化合物の濃度をモル濃度で表したものであり、アンモニウムイオン含有量とは研磨用組成物中に溶存しているアンモニウムイオンの総量をモル濃度で表したものである。例中、炭酸化合物として炭酸のアンモニウム塩を用いている例においては、アンモニウムイオン含有量は、炭酸のアンモニウム塩から放出されるアンモニウムイオンも含むものである。

【００４７】＜研磨試験＞次に、実施例１～９および比較例１～３の試料による研磨試験を行った。被加工物としては、ＣＶＤ法により二酸化ケイ素膜を成膜した６インチ・シリコンウェーハ（外径約１５０ｍｍ）の基盤を使用し、二酸化ケイ素膜の膜付き面を研磨した。

【００４８】研磨は片面研磨機（定盤径５７０ｍｍ）を使用して行った。研磨機の定盤には不織布パッド（Ｒｏ

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del社（米国）製Suba400）上に発泡ウレタンパッド（Rodel社（米国）製IC－1000）を貼り合わせた研磨パッドを貼り付け、二酸化ケイ素膜付ウェーハを装填して3分間研磨した。

【0049】研磨条件は、加工圧力490g／cm²、定盤回転数35rpm、研磨用組成物供給量150cc／分、ウェーハ回転数70rpmとした。

【0050】研磨後、ウェーハを順次洗浄、乾燥した後、ウェーハの膜厚減、すなわち研磨による取代を49点測定し、それを平均して研磨時間で除することにより、各試験別に研磨速度を求めた。

【0051】上記により求められた49点の取代から、次式により研磨面の均一性の評価基準であるN－Uを求めた。

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N－U（%）＝｛R.(max)－R.(min)｝／｛R.(ave)×2｝×100

上式において、R.(max)は最大取代、R.(min)は最小取代、またR.(ave)は平均取代を表している。

【0052】この式からも明らかなように、N－Uとは研磨において発生する膜厚減のばらつきによるウェーハ表面の凹凸、すなわち取代の不均一性を表す指標である。このN－Uの値が大きい研磨面ほど研磨による取代のばらつきが大きく、逆にN－Uの値が小さい研磨面ほど研磨による取代のばらつきが小さい。

【0053】

表1

	アンモニア含有量〔mol/l〕	炭酸化合物	炭酸化合物濃度〔mol/l〕	研磨速度〔nm／分〕	N－U〔%〕
実施例1	0.0215	炭酸アンモニウム	0.0086	152	4.6
実施例2	0.0347	炭酸水素アンモニウム	0.0086	153	6.0
実施例3	0.0347	炭酸アンモニウム	0.0086	153	6.3
実施例4	0.0347	炭酸アンモニウム	0.0172	158	6.8
実施例5	0.0614	炭酸アンモニウム	0.0086	156	10.0
実施例6	0.0614	炭酸アンモニウム	0.0172	159	10.1
実施例7	0.0614	炭酸アンモニウム	0.0009	149	10.7
実施例8	0.0951	炭酸アンモニウム	0.086	155	11.5
実施例9	0.1305	炭酸アンモニウム	0.086	160	12.7
比較例1	0.0347	－	－	124	6.6
比較例2	0.3071	－	－	143	15.2
比較例3	0.6550	－	－	144	19.4

【0054】表1に示した結果より、従来の研磨用組成物は、本発明の研磨用組成物に比較して、研磨速度が著しく小さいか、N－Uが著しく劣っており、本発明の研磨用組成物は優れた研磨速度と優れた研磨面の均一性とを両立していることがわかる。

【0055】なお、上記の表1において掲載しなかったが、これらの試験で用いた研磨済加工面を目視にて評価したところ、実施例、比較例ともに、スクラッチおよびその他の表面欠陥については見出されなかった。※

※【0056】

【発明の効果】本発明の研磨用組成物は、研磨速度が大きく、均一性が優れた研磨面を形成させることができること、さらに本発明の半導体ウェーハの研磨方法は、ウェーハ内の均一性が優れた研磨表面を形成させることができて、半導体ウェーハの生産性を向上させることができること、は、［発明の概要］の項に前記したとおりである。

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